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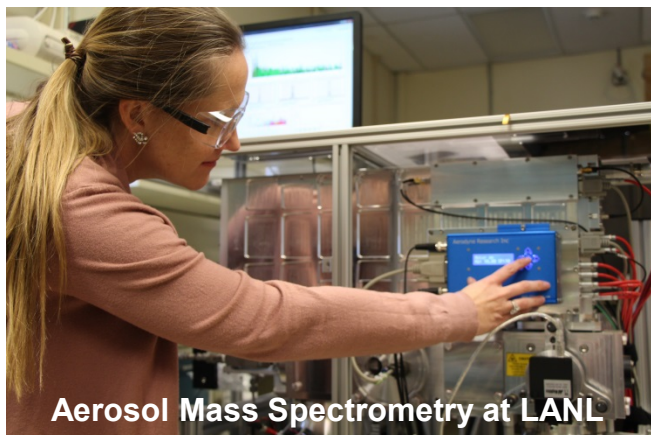
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Title:	Submicron Aerosol Chemical Composition and Optical Properties: In Situ Field Measurements and Controlled Laboratory Studies to Probe Dynamic Particle Processes for Climate
Author(s):	Aiken, Allison C.
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Submicron Aerosol Chemical Composition and Optical Properties: *In Situ* Field Measurements and Controlled Laboratory Studies to Probe Dynamic Particle Processes for Climate



Aerosol Mass Spectrometry at LANL



AMF1 on Ascension Island (ASI)



Wildfire Data: Las Conchas, NM

Allison C. Aiken
EES-14: Earth System Observations

Furman University, Chemistry Department

June 19, 2019

Personal Background

- **Undergrad. Research Assistant, 1999: Furman**
 - NSF-REU Watershed Research with John Wheeler
- **Undergrad. Research Assistant, 2000, 2001: LANL**
 - Furman Research Fellowship, 2000 with Tony Arrington
- **BS, BS, 2002: Furman University**
 - Chemistry, ACS Certificates in Chemistry and Environmental Chemistry
 - Biology, field ecology
- **PostBaccalaureate Research Assistant, 2002-2003: LANL**
 - C-PCS with Steve Buelow
 - Time-of-Flight Mass Spectrometry of Laser-driven fliers and a fluid dynamics model for shock dynamics



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Allison Aiken

Allison, who works for Steve Buelow in C-PCS, came to the Laboratory as a summer student and then returned as a post baccalaureate. Allison double majored in chemistry and biology. She completed her BS at Furman University in South Carolina. Allison will be here until July of 2003 and then is going on to grad school. She has been accepted by three universities and has not made a decision concerning which one to attend as of yet.

Allison's project is focused on physical chemistry, and she is also part of the Hercules team, which she explains:

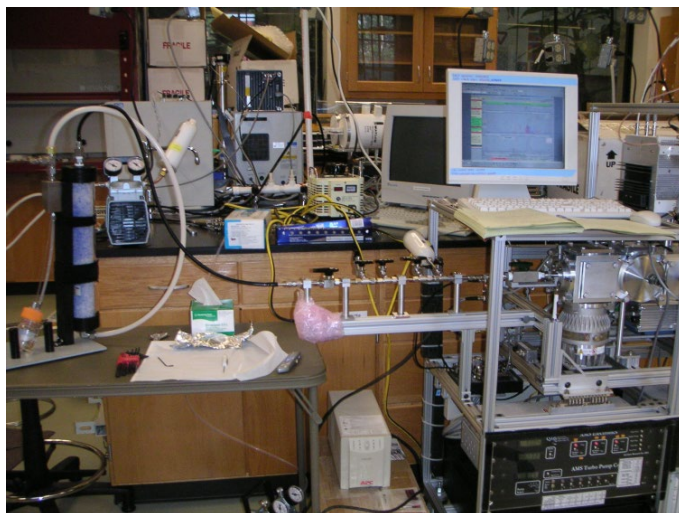
"HERCULES (High Explosives Reaction Chemistry via Ultrafast Laser Excited Spectroscopy) is a collaborative project being worked on with DX-2 to elucidate the chemistry and energy transfer dynamics that occur in the shock fronts of detonating materials. Our part of the project uses a laser driven flyer system to probe the chemistry on nanosecond to microsecond time scales. The flyers consist of aluminum and aluminum oxide (sometimes carbon-backed) placed on glass by chemical vapor deposition. The target being used is nitrocellulose spin-coated onto a stainless steel disk. The experiment has looked at positive and negative ions with a mass spectrometer, light, and total charge. Currently, we are focusing on the large negative charge detected with a probe directly touching the 1 um to 10 um nitrocellulose sample in an effort to eliminate any signal due to cracking."

Allison enjoys working for the Laboratory because she feels that she is surrounded by opportunity, and enjoys the freedom that students are given for research at the Laboratory.

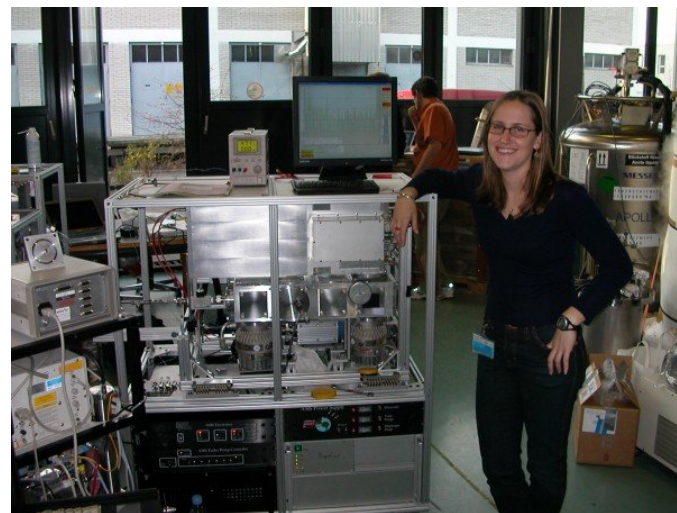
Allison enjoys skiing, snowboarding, hiking, swimming, and drawing in her spare time.

Personal Background

- **PhD, 2008: University of Colorado at Boulder**
 - Analytical/Atmospheric Chemistry with Jose-Luis Jimenez
 - NASA Earth System Science Graduate Student Fellowship
 - Thesis: Quantitative Chemical Analysis of Urban and Source Organic Aerosols Using High-Resolution Aerosol Mass Spectrometry
 - 50/50 Laboratory work and Field Campaign Measurements

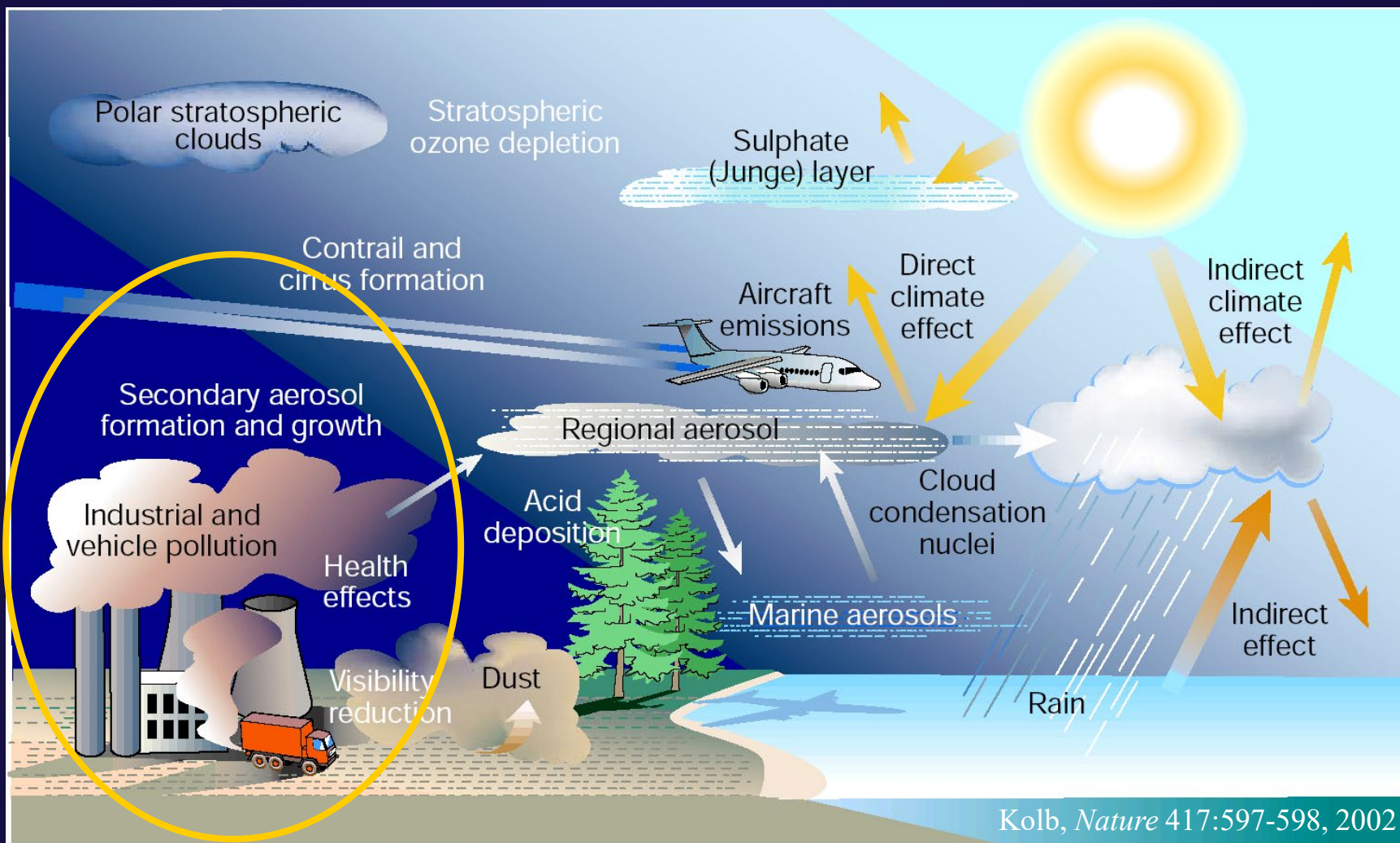


CU-Boulder
Elemental Analysis Experiments



Paul Scherrer Institute (PSI)
Smog Chamber in Switzerland
Secondary Organic Aerosol

Why Study Atmospheric Aerosols?



Goal: Decrease uncertainties with direct measurements (size, composition, optical properties, and concentration)

Ambient Aerosols: Impacts on Climate

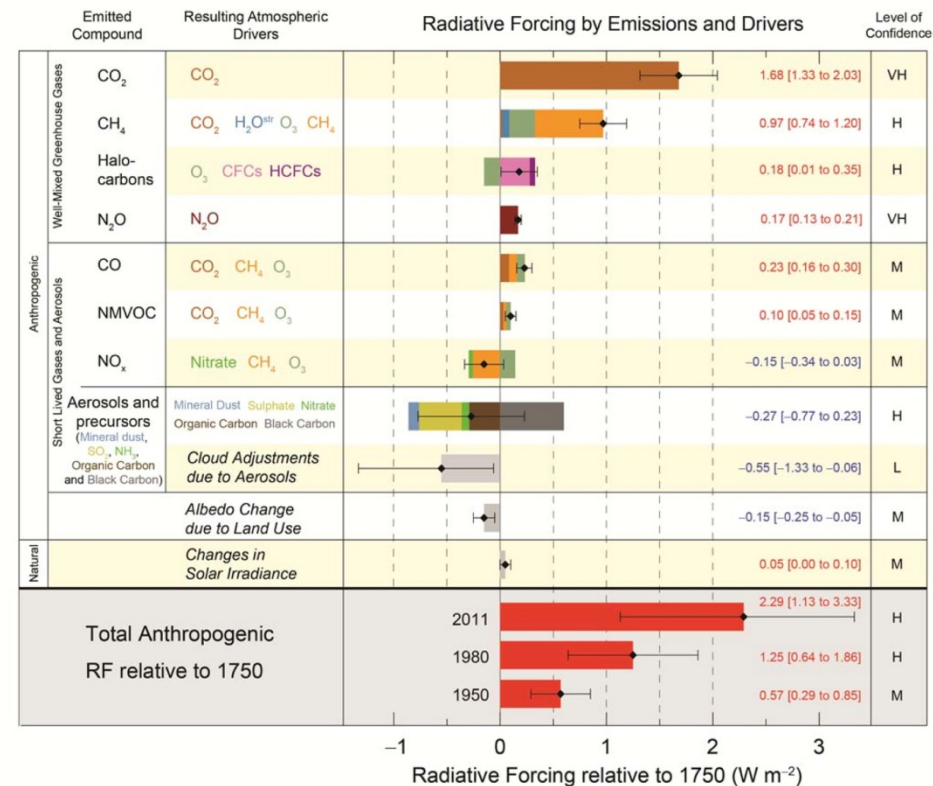
■ Greenhouse Gases – Terrestrial Warming from CO₂

■ IPCC Aerosol Radiative Forcing

- First thought to be cooling and dominated by sulfates
- 2007: Largest uncertainty is still in the aerosols
- 2013 (AR5): BC absorption slightly increased (0.6 W m⁻²)

■ Chemical Information

- Most Aerosols absorb while others cool the atmosphere
- **Black Carbon:** 2nd most important factor in global warming (behind CO₂) & most uncertain (*Bond et al., 2013*)
- Sulfate and Organics – Cooling



IPCC, AR5, 2013.

Why Study Aerosol Chemistry?

Color Code:

Organics

NH₄

NO₃

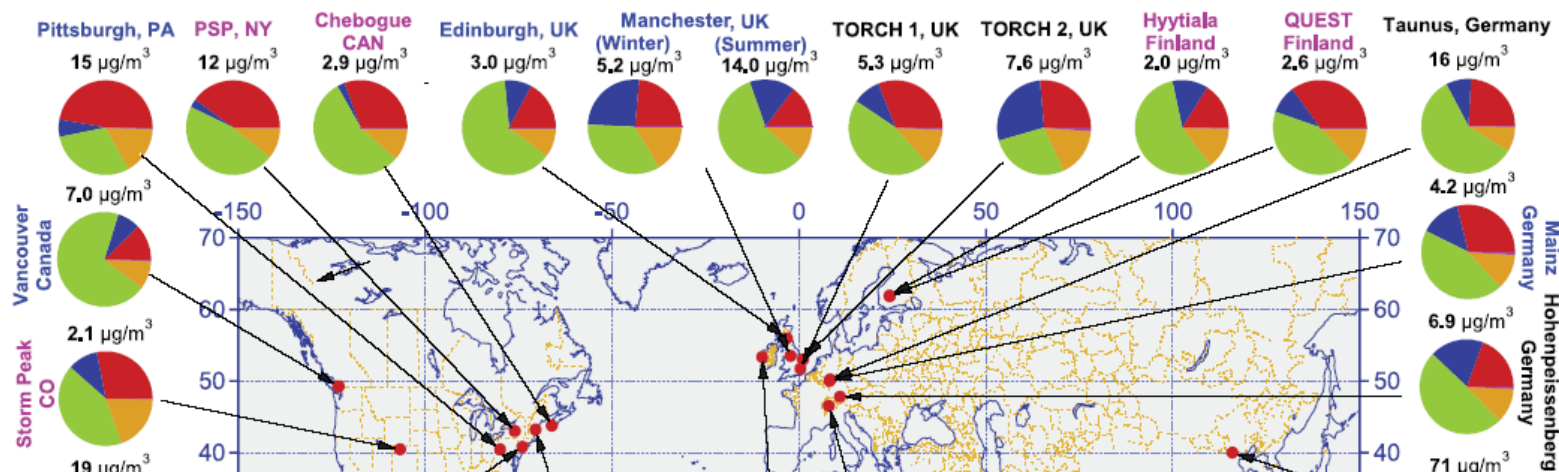
SO₄

20-90% of the particle mass from organics

Effects on climate, human health, etc...

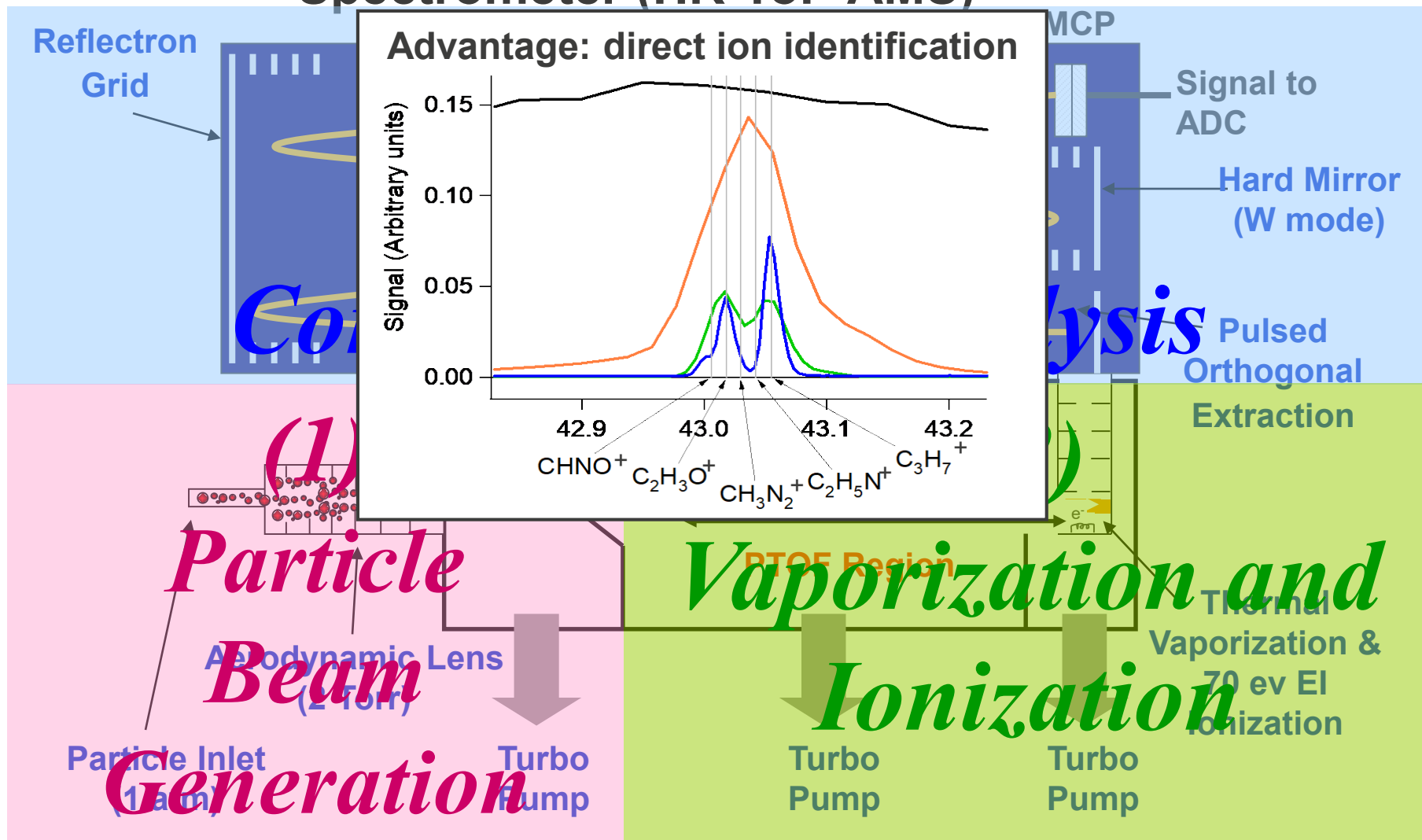
Global sampling of particles < 1 micron diameter

Q. Zhang et al, Geophys. Res.Letters, 2007



- What are these OA?
 - Thousands of species
 - Extreme range of properties: MW, vapor pressure, functionality, polarity, hydrophilicity:
 - Hydrocarbons, aldehydes, ketones, peroxides, polyacids, oligomers, humic-like substances...
 - No technique or combination can analyze all OA at the compound level
 - Typical GC-MS: off-line, 6-24 hrs averages, 10% of the organic mass
 - Traditionally poorly characterized

High Resolution Time-of-Flight Aerosol Mass Spectrometer (HR-ToF-AMS)

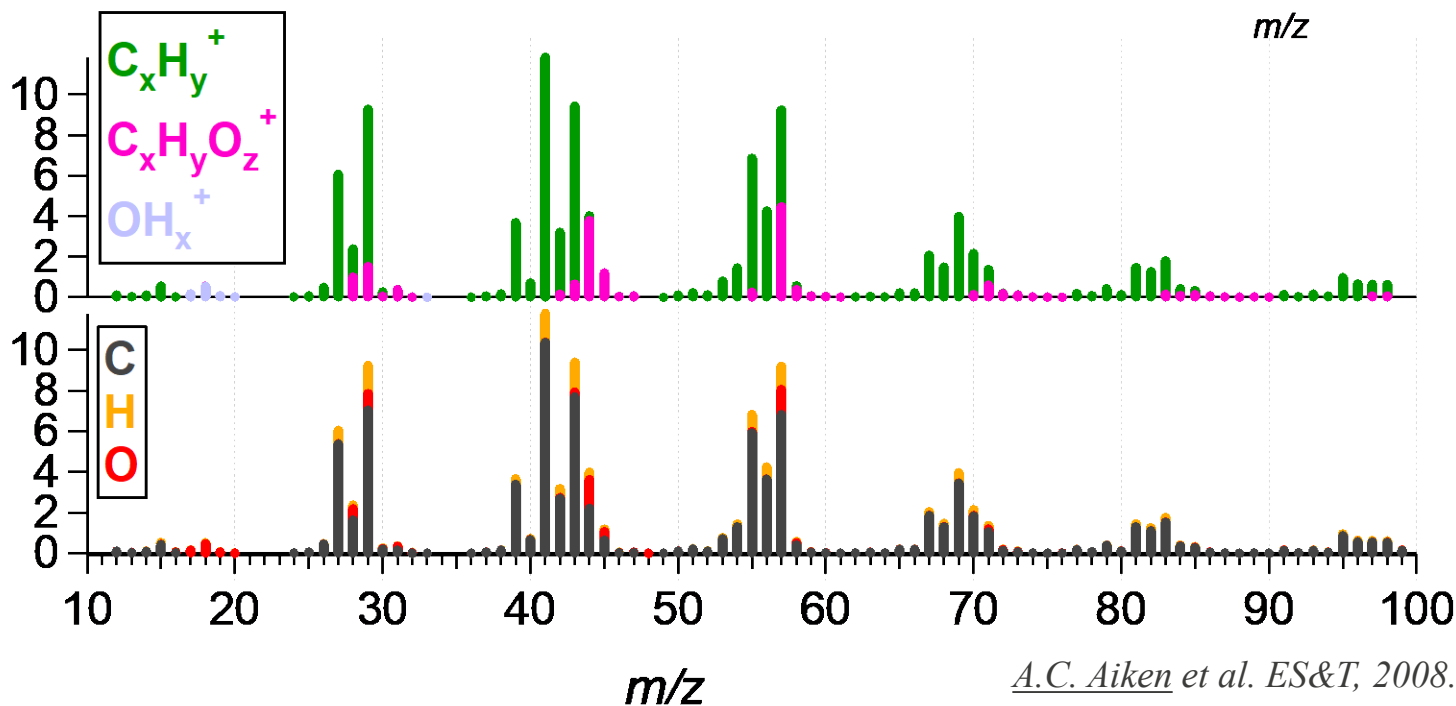
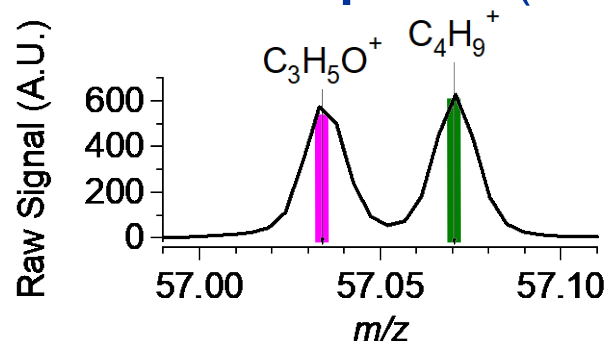


P.F. DeCarlo, J.R. Kimmel, A. Trimborn, M.J. Northway, J.T. Jayne, A.C. Aiken, M. Gonin, K. Fuhrer, T. Horvath, K. Docherty, D.R. Worsnop, and J.L. Jimenez. Field-Deployable, High-Resolution, Time-of-Flight Aerosol Mass Spectrometer. *Analytical Chemistry*, 78: 8281-8289, 2006.

Elemental Analysis (EA) by EI-HRMS

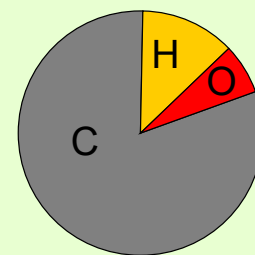
- EI MS Ion intensities \propto original mass
 - *Crable and Coggeshall, Anal Chem, 1958; Jimenez et al., JGR, 2003*
- Identify all ions (HRMS)
- Determine Elemental Mass
 - Atomic and Mass Ratios

Nonanal spectra (AMS)



Atomic Ratios:

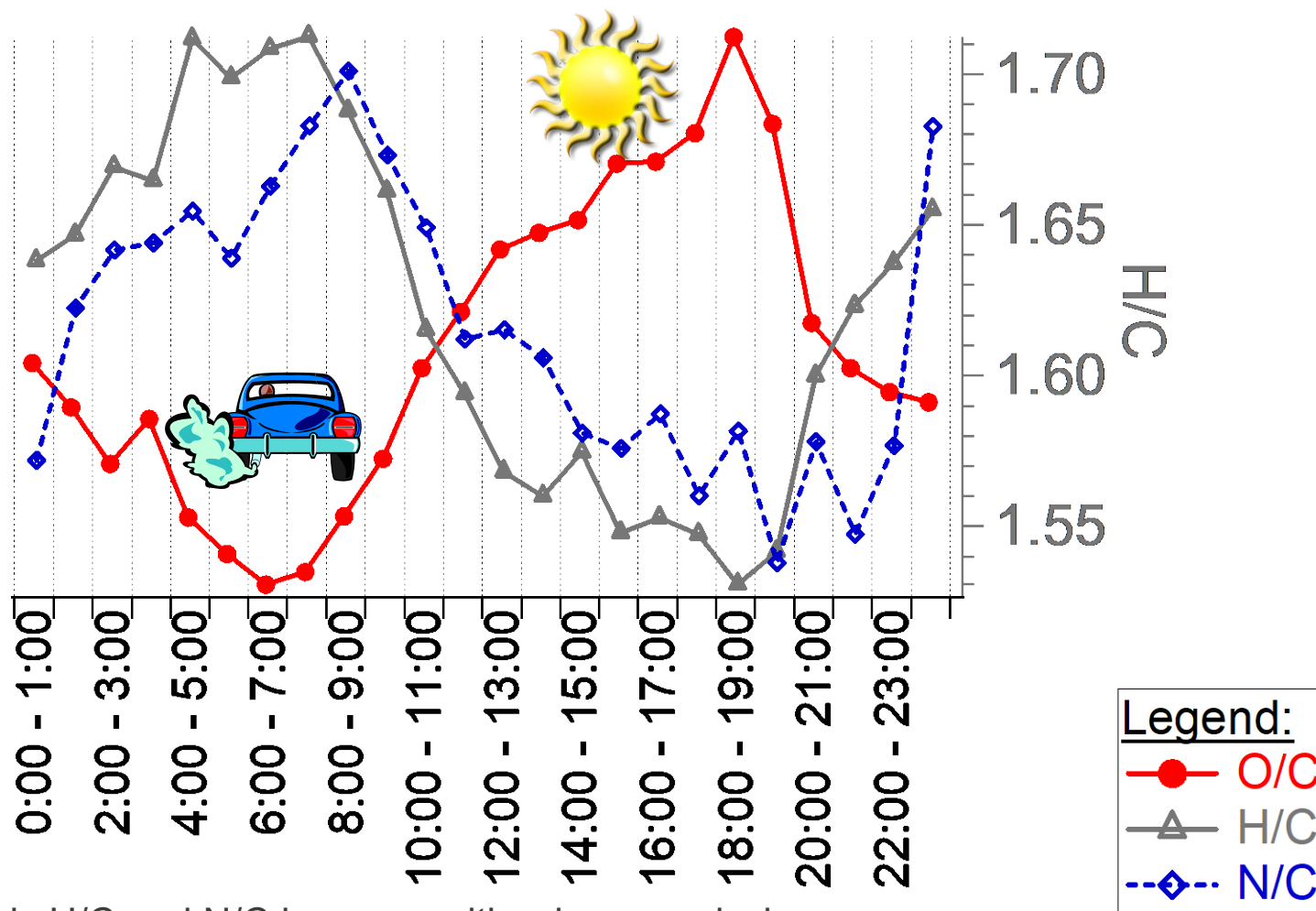
	O/C	H/C
Molec	0.11	2.0
Calc	0.06	1.8



A.C. Aiken et al. ES&T, 2008.

Advantages of Real-Time Direct Aerosol Measurements

Elemental Analysis: Mexico City



- Atomic H/C and N/C increase with primary emissions
- Atomic O/C increases later in the day with production of secondary species

Black Carbon (a.k.a. “soot”) – Sources and Impacts

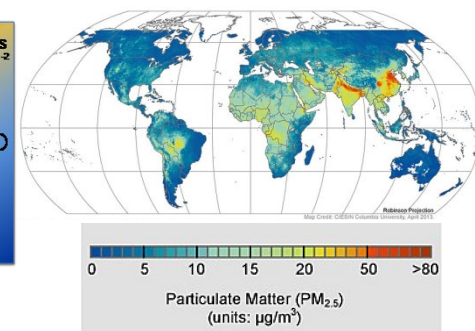
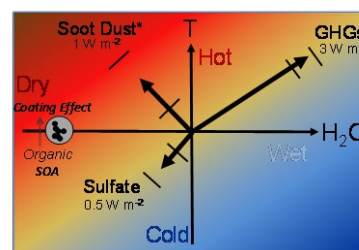
• Sources

- Incomplete combustion of fossil fuels, biofuels, biomass
- Ex: diesel/gas emissions from vehicles, coal-fired power plants, cook stoves, wildfires, trash burning, residential wood burning
- Small particles ($PM_{2.5} < 2.5 \mu m$ diameter)



• Climate Impacts

- Directly warms the atmosphere
- Indirectly can contribute to decreased precipitation and changes in cloud albedo
- Increase ice/snow melt by deposition
- Decreases air quality and visibility



• Human Health

- Asthma and respiratory illness
- Cancer and cardiovascular disease
- Decreased lifespan



Climatic Effects from Black Carbon and Coatings

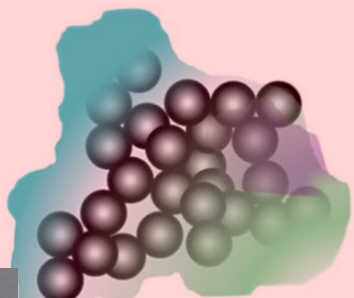
- Important yet highly uncertain factor in global warming (Bond et al., 2013)

Questions: What is the morphology of BC?

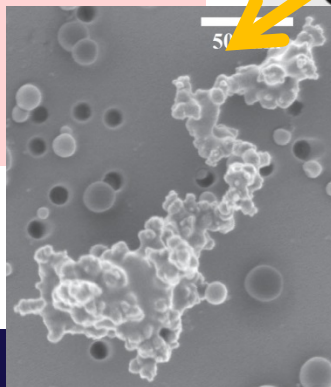
Does it result in enhanced BC absorption?

- 4 Types of BC from SEM Images during Las Conchas
(China et al., *Nature Communications*, 2013)
- BC Morphology is important for modeling climate and BC absorption

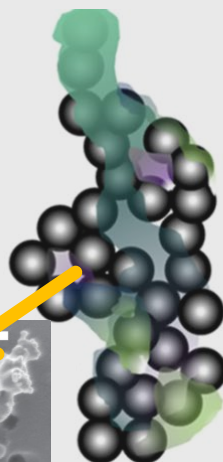
Thickly Coated BC



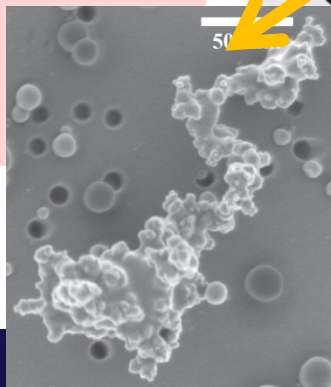
500 nm



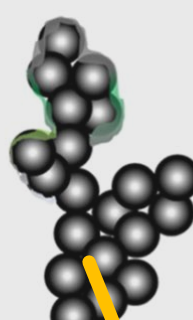
Thin BC



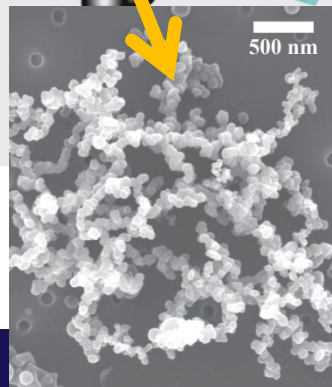
500 nm



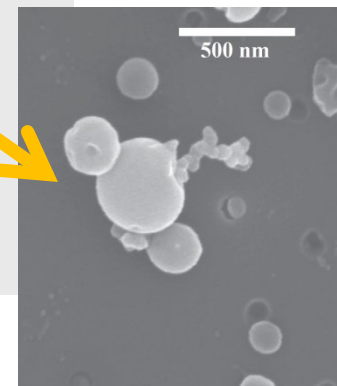
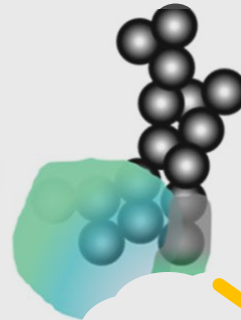
Bare BC



500 nm



BC Inclusion



BC in a “Fresh” Wildfire Plume

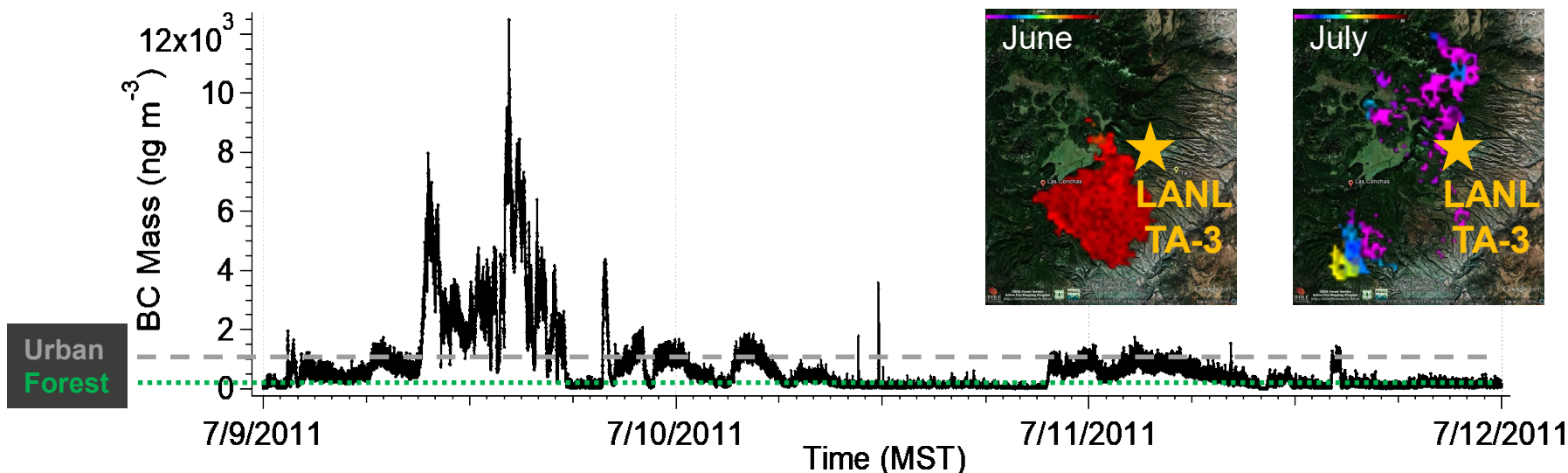
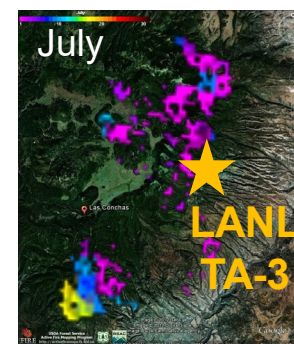
Las Conchas Wildfire (June – August 2011)

- 2nd Largest NM Fire (largest at the time)
 - ~157K acres burned, started ~10 miles W of LANL
 - ~10% of the particles contain BC
- “Fresh” BC concentrations $> 10 \mu\text{g m}^{-3}$
 - After Containment (during, est. $10\times \sim 100 \mu\text{g m}^{-3}$)
 - ~10x Urban Pollution (Liu, [Aiken](#) et al., *Nature C.*, 2015)
 - ~200x “clean” Forest ([Ortega...](#) [Aiken](#) et al., *ACP*, 2014)
- ~1-3 hours atmospheric aging

Image from the International Space Station (ISS)



USDS MODIS Fire Burn Scars

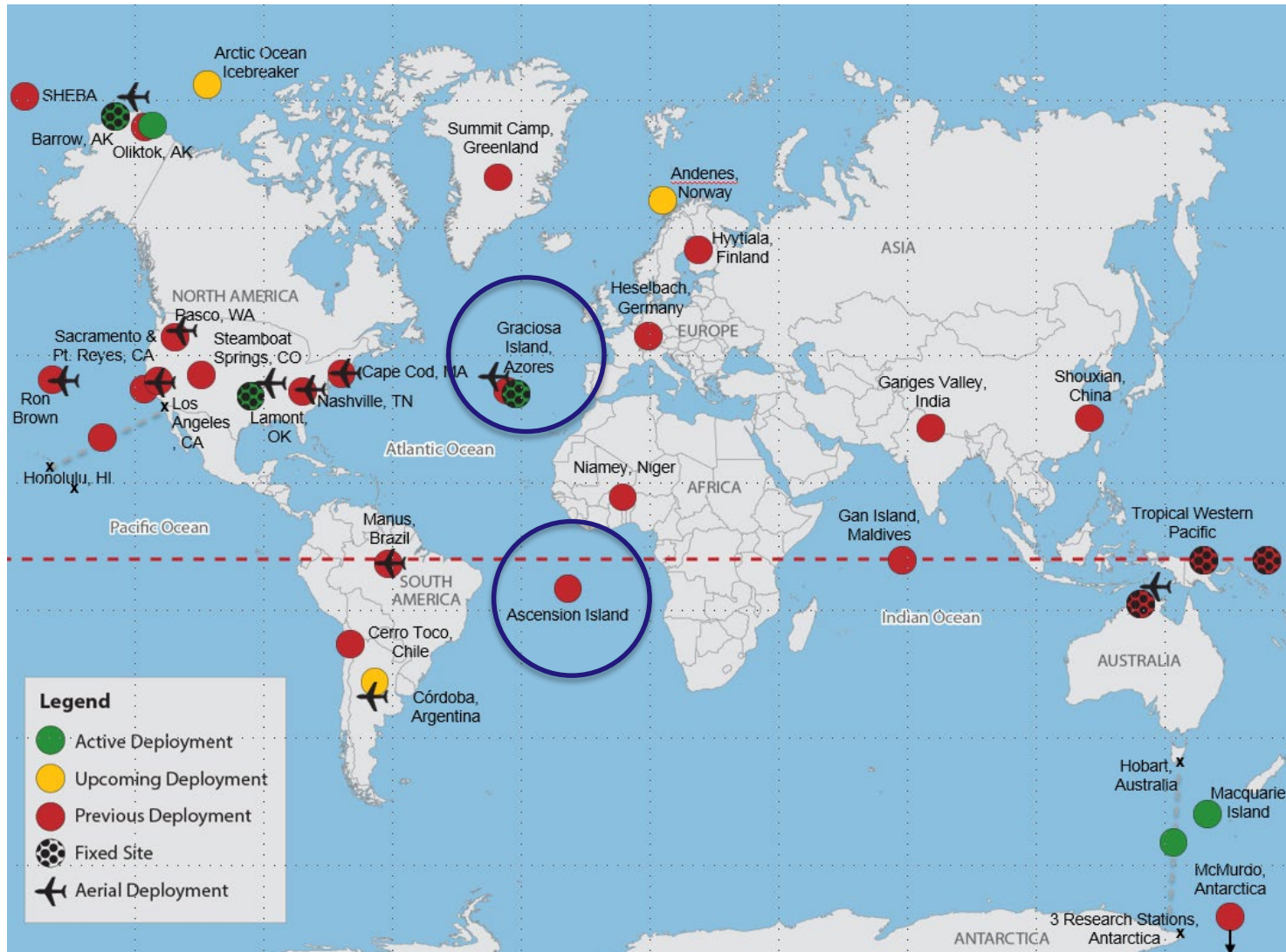


Missoula USFS Fire Sciences Lab Stack Burns



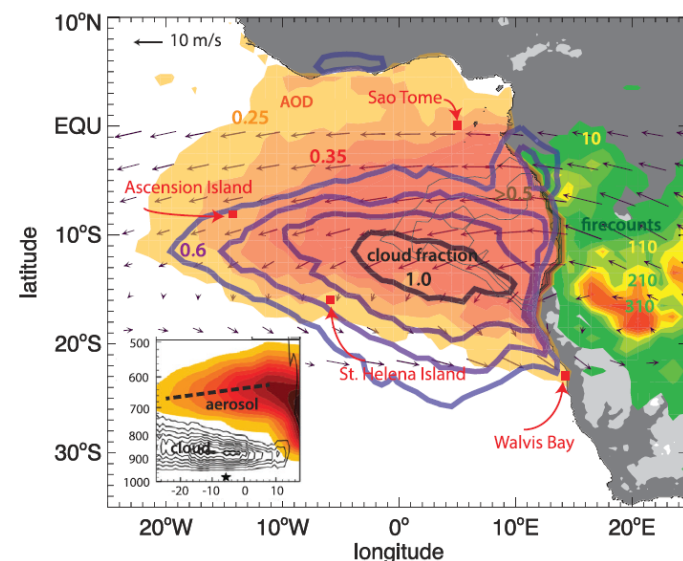
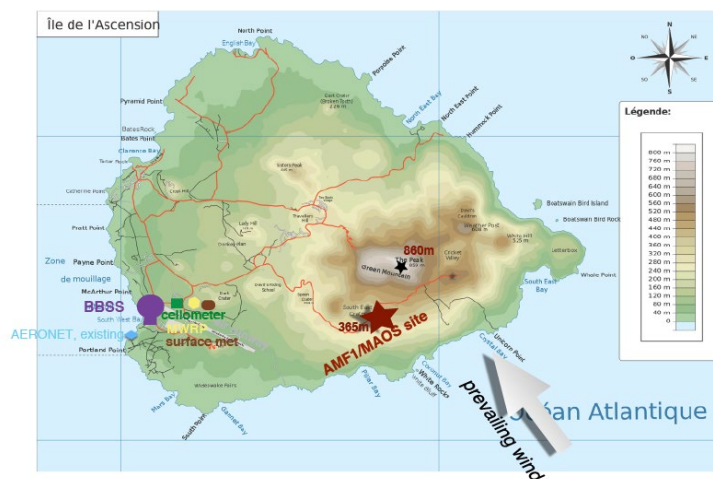
- Stack Burns: Fuels are burned at the ground and the emissions are pulled up the stack by using a low pressure inside the stack
- Gas-phase and aerosol measurements are made from a platform at the top of the stack ~50 ft above the fire

U.S. Department of Energy Atmospheric Radiation Measurement (ARM) Facility



Layered Atlantic Smoke Interactions with Clouds (LASIC)

- **Southern Africa and Biomass Burning (BB)**
 - Largest source of BB Emissions Globally
 - Land Clearing Wood and Grassland Fires
 - BB Season is from June to November
- **LASIC Measurements**
 - Ascension Island in the Southern Atlantic Ocean
 - June 2016 – Oct. 2017
 - Two Southern African BB Seasons



P. Zuidema, BAMS, 2016

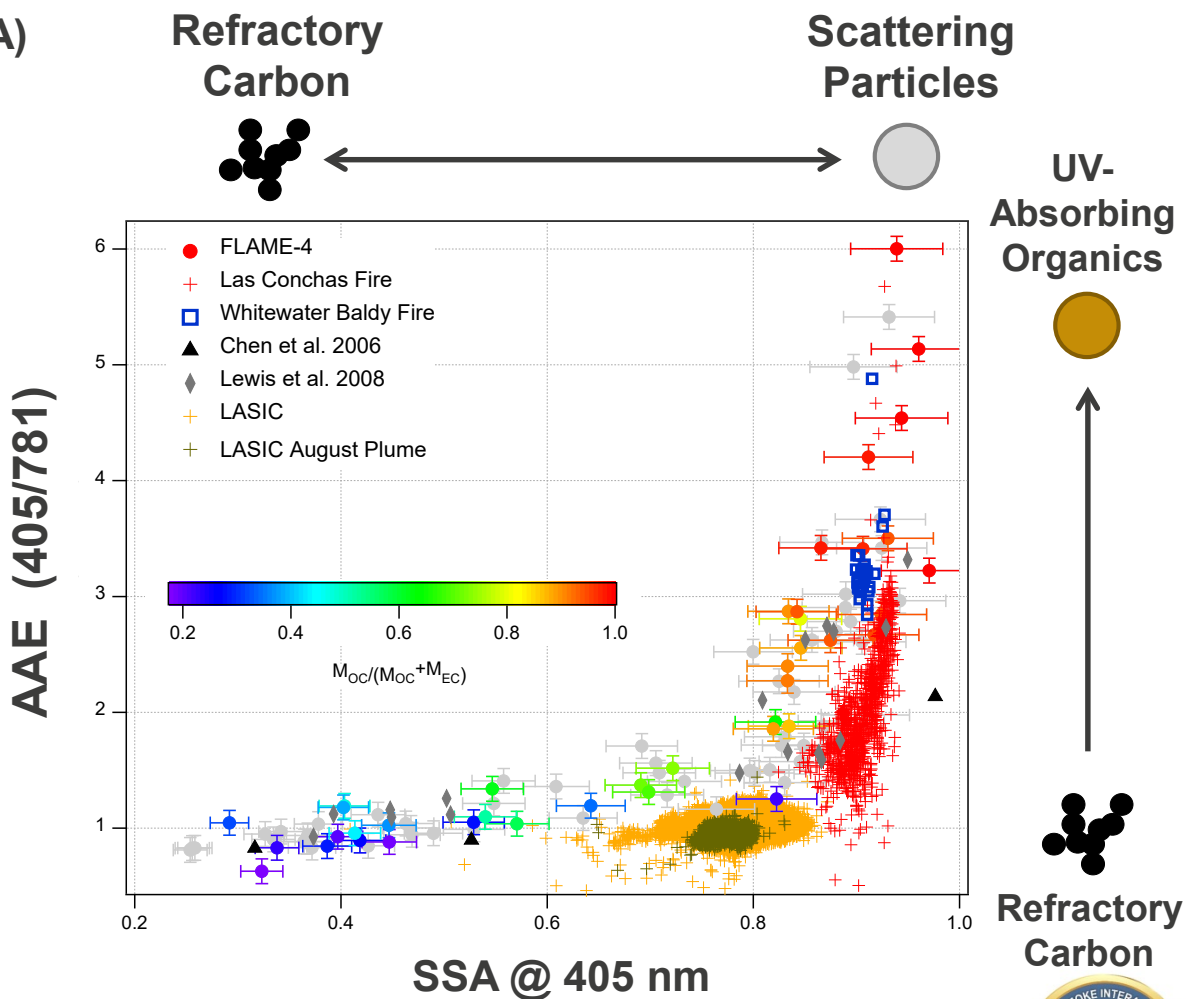
ARM Mobile Facility (AMF1 with AOS and MAOS) at LASIC

- **Aerosols and Trace Gases in the Aerosol Observing System (AOS) and Mobile AOS (MAOS)**
 - Surface: Particle number, size, optical properties, refractory Carbon (rC) content, non-refractory chemical composition, hygroscopicity and water uptake properties, Nitrogen Oxides, Combustion tracers (CO , SO_2), Ozone, Volatile Organic Compounds
 - Column: Sunphotometer
- **Atmospheric Profiling**
 - Microwave, High Frequency, and 3-Channel Radiometers
- **Clouds**
 - Lidar, Cloud Radars (K- and W-band) Total Sky Imager, Ceilometer
- **Radiometers**
- **Surface Meteorology**



LASIC Biomass Burning Organic Aerosol Comparison to Laboratory and Near-field Biomass Burning Data

- **X: Single Scatter Albedo (SSA)**
 - Values from 0 - 1
 - Bare refractory Carbon ~ 0.4
 - Scattering Organics ~ 1.0 (non-absorbing)
- **Y: Absorption Angstrom Exponent (AAE)**
 - Refractory Carbon ~ 1.0 (λ independent)
 - Absorbing organics > 1 (higher in the UV)
- **Ambient US Forest Fires**
 - SSA $\sim 0.85 - 0.95$
 - AAE $\sim 1 - 4$
- **LASIC**
 - Lower SSA (0.81 ± 0.03) and AAE (1.04 ± 0.10)
 - Refractory Carbon dominates, no evidence for organic absorption



S. Liu, A.C. Aiken, et al., GRL, 2014



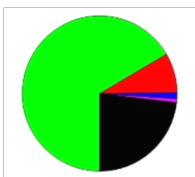
LASIC Biomass Burning Plume Chemical Composition

- Non-Refractory Submicron Aerosol Mass
 - Dominated by Organics
- Total (non-refractory + refractory Carbon)

August

$2.2 \mu\text{g m}^{-3}$

Org/rC = 3.0



Organics = 67.0%

Sulfate = 8.59%

Nitrate = 1.37%

Chloride = 0.78%

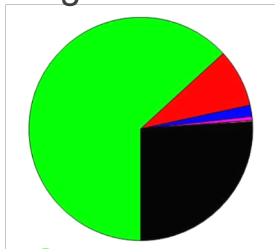
Ammonium = -0.01%

rC = 22.3%

8/7 – 17 Plume

$3.9 \mu\text{g m}^{-3}$

Org/rC = 2.4



Organics = 63.2%

Sulfate = 8.39%

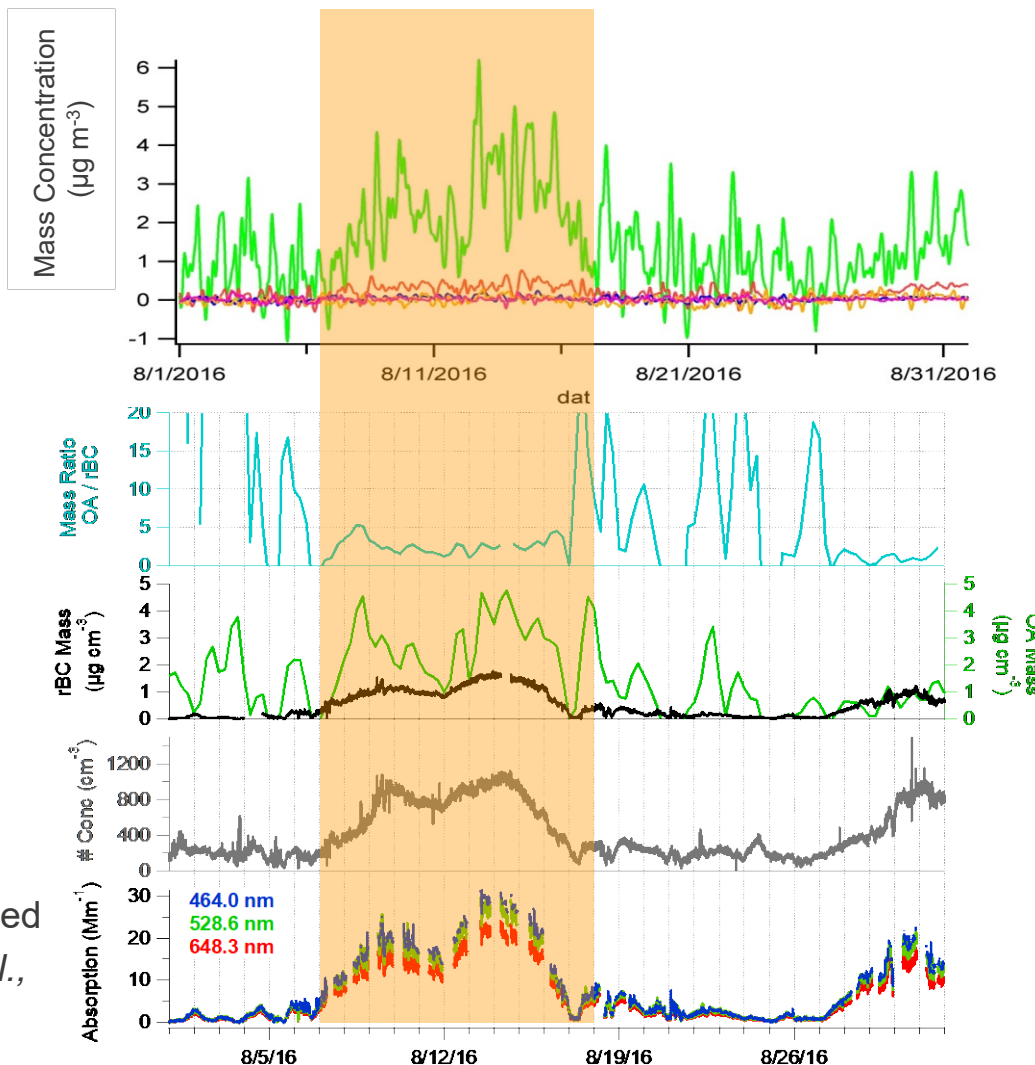
Nitrate = 1.61%

Chloride = 0.58%

Ammonium = 0.20%

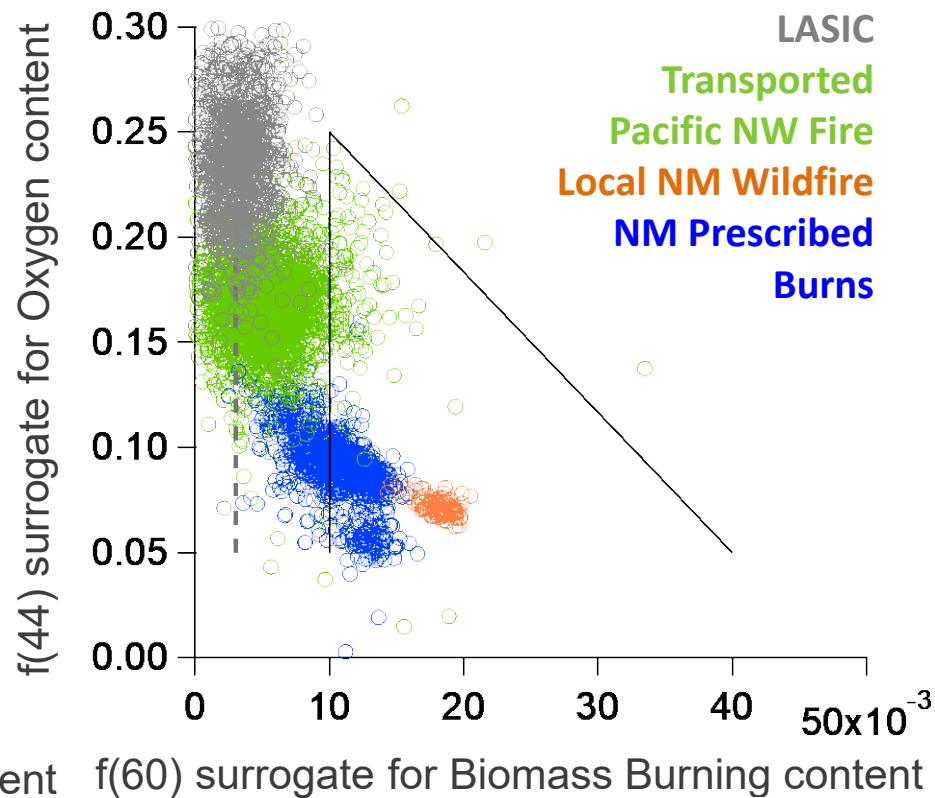
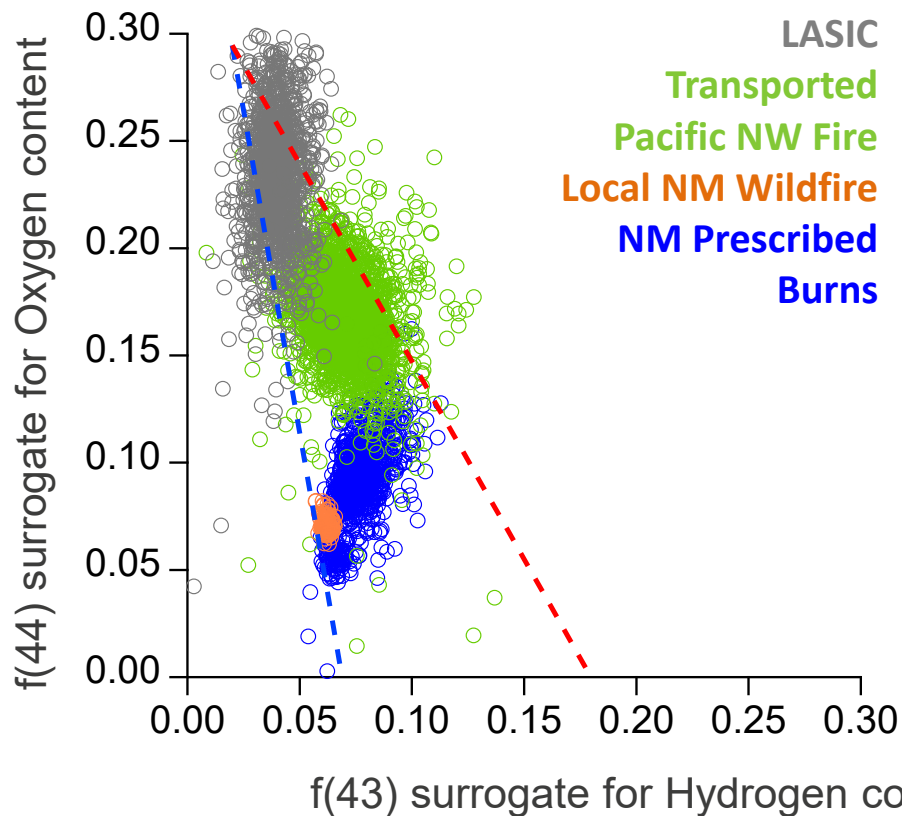
rC = 26.0%

- Preliminary (PMF) Analysis
 - Most of the Organics are Aged/Oxidized
 - Aged Biomass Burning - *S. Zhou et al., ACPD 2016*
- Bulk Chemical Information
 - Refractory Carbon and Organics dominate

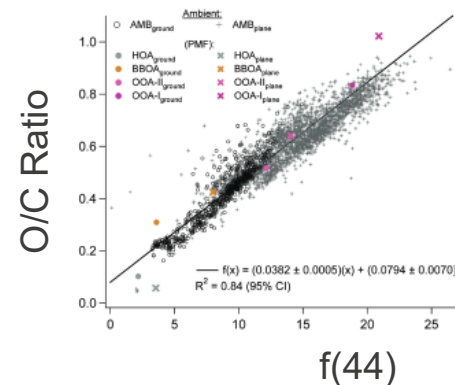




LASIC Biomass Burning Organic Aerosol Comparison to 2017 US Wildfire Data



- **LASIC Elemental Analysis Approximation**
- Aiken et al., ES&T, 2008
 - **O/C = 0.98 ± 0.12**
 - **OM/OC = 2.41 ± 0.16**



Conclusions

- **Absorbing Aerosols directly warm the atmosphere**
 - Black carbon – strongest absorber, most well known, but varies due to internal mixing and aging in the atmosphere
 - Brown carbon, absorbing dusts – most uncertain
 - Aged biomass burning observed at Ascension Island from Southern Africa (dominated by soot)
- **High variability in direct radiative forcing of Absorbing Aerosols**
 - Large differences – fuels, atmospheric aging, etc.
 - BC absorption enhancements due to coatings and direct absorption from Brown Carbon observed in the Winter in the UK
- **Aerosol Mass Spectrometry**
 - Real-time *in situ* measurement of soot and organics, including chemical changes (oxygen-content) in real time
 - Local wildfires sampled
 - Climate and Forensic applications
- **Need for ambient aerosol *in situ* measurements**
 - Sample regional and source-specific differences
 - Closure studies
 - Capture dynamic processes

Acknowledgements and Funding

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- Kyle Gorkowski – now at McGill, Montreal
- Claudio Mazzoleni – Michigan Tech. University
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- Leah Williams, Doug Worsnop, Tim Onasch – Aerodyne, Billerica, MA

